History and Development of the Deposition of Copper Ferrocyanide Membrane by the Electrolytic Method

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY
CHESTER NEWTON MYERS
BALTIMORE
1910

EASTON, PA.:
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The author desires to express grateful acknowledgment to Professor Morse for his kindly assistance and experienced supervision in this investigation. His inspiration and valuable instruction in careful manipulation call for appreciative recognition. To President Remsen for his valuable instruction in the lecture room and the pleasant memories connected with his lectures are due the gratitude and recognition of the author. No less are Professors Acree, Jones, Ames and Bliss worthy of recognition. The author also wishes to use this opportunity of expressing thanks to the earlier co-workers of Prof. Morse for valuable suggestions obtained from their publications. To Dr. Holland for his untiring assistance and suggestions, great appreciation is due.

History and Development of the Deposition of Copper Ferrocyanide Membrane by the Electrolytic Method.

It is quite unnecessary, in giving an historical account of the work done on semipermeable membranes, to mention more than briefly, the work and investigations of Pfeffer, the theoretical conclusions of van't Hoff founded upon Pfeffer's determinations, the results of Tammann, Hamburger, and De Vries, men working upon van't Hoff's brilliant conclusions. Such were the investigations and conclusions which showed the scientific world the great importance of the subject with which we are now dealing. Notwithstanding the almost insurmountable difficulties of the work, later progress has corresponded to these brilliant beginnings.

No work comparable to that of Pfeffer's has ever been done, following the methods of this investigator, but a new method has come to the front, replaced an old one, given results which are in a class by themselves for accuracy and originality of determination. This practical method of membrane deposition and its application to the work was devised by Morse and Horn, improved upon by Morse and his later co-workers. To them, we owe the first ideas of electrolytic deposition of the semipermeable membrane in the walls of a porous cup.

In the original article of Morse and Horn, they state the object they had in mind in the following words: "It occurred to the authors that if a solution of copper salt and one of potassium ferrocyanide are separated by a porous wall which is filled with water, and a current is passed from an electrode in the former to another electrode in the latter solution, the copper and the ferrocyanogen ions must meet in the interior of the wall and separate as copper ferrocyanide at all the points of meeting, so that in the end there should be built up a continuous membrane well supported on either

side by the material of the wall." Such were the first conceived ideas in the progress of the methods of membrane formation.

The first problem which confronted the efforts of this early work was a method of effectively removing the air from the porous cups which, in themselves, furnished but a poor means of supporting the copper ferrocyanide membrane. The purpose of removing the air from the walls of the cell is obviously to overcome the interference in the formation of a sound and homogeneous membrane. The investigators made use of the strong endosmose which appears, when a current is passed through a porous wall, separating two liquid substances. The Morse-Horn method of removing the air from the walls of these porous cups, consisted in the use of a boiled solution of potassium sulphate containing about five-tenths of a gram of salt in a liter of water. This sulphate solution is placed both in the interior of the porous cup and in the jar in which the cup sits. On passing the current between the electrodes in the direction of the electrode within, the liquid in the cup rises with a sufficient rapidity to increase with the dilution of the solution and with the intensity of the current. As the liquid is carried along by the electric current, the air is bodily swept along with the water to the interior of the cell and thence out of the siphon.

The electrodes used for this work are platinum. The inner electrode is fastened to the platinum wire which passes through the rubber stopper. This rubber stopper contains a funnel which admits solution to the interior of the cell and a side tube which serves as an outlet and part of the siphon. As this endosmose takes place, it is found that water and air pass through very rapidly at first. The sulphate is added to the jar occasionally, and the electrolysis is continued until about three hundred cc. of the sulphate has passed out through the siphon. This is found to be sufficient to remove all air that may have been included within the walls of the cell. According to this method, the cells were then placed in a large volume of distilled water

to remove the salt that had accumulated in the walls of the cell.

"To form the membrane, the wet cup was placed in a beaker and surrounded with an electrode of sheet copper, which completely encircled it. The other electrode—the one within the cup—was of platinum. After fixing the electrodes and connecting with a dynamo, so that the current should begin to flow the instant the liquids touched the opposite walls of the cup, the copper solution ($N/10$ or $N/5$ sulphate) and that of potassium ferrocyanide ($N/10$ or $N/5$) were introduced as nearly simultaneously as possible. At first, there is considerable endosmose in the direction of the current, *i. e.*, from the copper solution into that of the ferrocyanide, but no copper has ever been found to enter the cup, neither have any of the ferrocyanogen ions made their way into the copper solution. The resistance usually rises quite rapidly, reaching in extreme cases three thousand ohms within an hour, while the endosmose decreases correspondingly. The most rapid rise in resistance is observed in the less porous, hard burned cells. In softer and more porous ones, the resistance may not exceed two hundred to three hundred ohms within an hour; and after a time, in such cases, the resistance begins to fall, owing, apparently, to the action of the accumulated alkali upon the membrane. If the solution of ferrocyanide in the cell is then replaced by a fresh one, the resistance begins to rise again." Such were the observations of Morse and Horn in their original paper.

In the earlier work it was regarded improbable that the osmotic pressure of concentrated solutions could be measured because a *satisfactory* membrane could not be deposited by electrolysis. The difficulty which manifested itself was in the fact that the walls of the cell may contain cavities of such size as to interfere with the best results of membrane formation, in that it is necessary for a "key" to attach the membrane to and then to pack sufficiently a membrane of considerable volume, attached only at a few points. During this stage of the investigation it was found that the walls

of the cell must be very compact to start with, then this cell should be burned so that it was very hard. A cell of close texture, however, is found to be an essential feature for a cell of good quality.

Having thus obtained a cell of this character, the next step is to prepare it for the membrane-forming process. The method, formerly employed, consisted in passing a solution of potassium sulphate through the cell and then by endosmose, allowing water to remove any accumulated salt from the walls of the cell. This endosmose is continued until the liquid conducts the current very poorly. The cell is now ready for membrane deposition. To deposit the membrane, the following procedure is employed: A long platinum rod, which serves as the cathode, is lowered into the cell, and a cylinder of copper in copper sulphate solution is used as the anode. Into the cell, there is inserted a siphon, which reaches nearly to the bottom of the cup. The purpose of this siphon is to remove the liquid from time to time in order to prevent the accumulation of alkali, which is believed to be injurious to the membrane. For this deposition, an $N/10$ ferrocyanide solution and an $N/10$ copper sulphate solution are introduced into the cup, the former being placed in the interior of the cup, the latter being placed in the jar in which the cup rests. During the process of actual measurement, potassium ferrocyanide and $CuSO_4$ are used in the solutions for the purpose of mending the momentary ruptures in the membrane, caused by the increasing pressure.

Up to this time, membranes of copper ferrocyanide had received most attention, but at this stage of the work further research in regard to membranes was carried on. It was now found that the electrolytic method is well adapted to the deposition upon or within the walls of a cell of nearly every kind of precipitate which can be formed from electrolytes in solution. The ferrocyanides of tin, zinc, cadmium, manganese and uranyl; phosphates of the iron (trivalent), copper, and uranyl; hydroxides of aluminium and iron (trivalent); cobalti cyanides of cobalt, nickel, iron (bivalent), copper, zinc, cadmium, and manganese were shown to manifest

osmotic activity to a promising degree. These membranes should possess the properties of *insolubility*, *firm consistency*, *chemical inertness*, *permanency*, and most of all *osmotic activity* and *semipermeability*. These membranes, for the most part, possess these properties to a greater or less degree. It was found that cells of various textures were needed for different membranes.

As the progress of the work advanced, it was found advisable to use one-tenth normal solutions of copper sulphate and potassium ferrocyanide to deposit the membrane. In membranes of this class, it is found that alkali, which accumulates during the process of electrolysis, must be removed, owing to the deleterious effects upon the membranes. However, it was found that, in the case of the cobalti cyanide membranes, a little acetic acid can be used to prevent the accumulation of alkali. It was considered a too hazardous performance in the case of other membranes which showed great activity.

Voltages ranging from 110 volts to 250 were tried, but upon experimental evidence, it was found that voltages between 110 and 120 gave more satisfactory results than any other voltages. A greenish-black deposit was observed at higher voltages, instead of the formation of the cyanide membrane. The probable explanation is the decomposition of the membrane of copper ferrocyanide which is first formed. It is noticed that, when the circuit is first closed, the resistance is very high in some cases, due to the fact that there is an absence of the electrolyte in the cell wall—pure water. Soon, however, the current increases for a short time but falls rapidly after having reached this maximum. It is a result of experience that, if any further increase in current occurs, the cell should be taken down. To some extent the probable excellence of a cell is determined by its conduct during the membrane-forming process. The cell is now taken down, washed, and placed in distilled water before setting up for measurement.

Such has been the experimental stages through which the investigations passed. A description of the work of

preparing a cell which gave measurements in which considerable reliance might be placed, is now in order. The treatment previously described, was given the cells and the deposition of the membrane begun. It was noticed that the first membrane deposited rarely gave the highest pressure which is known to be normal for that solution. It thus becomes evident that a good membrane must be built up gradually. To do this, certain definite methods must be followed. A membrane is deposited; then it is rendered more compact by subjecting it to pressure developed by a sugar solution. It is taken down, washed, subjected to the membrane-forming process to repair any of the ruptures which have been produced and finally set up for packing again. This is repeated for a time sufficient to produce a compact, non-leaking membrane. This alternating rupturing and packing is continued until the ruptures are very small. At this stage another method of repair and mending is used. This is a simultaneous rupturing and mending process in which copper sulphate on the outside and potassium ferrocyanide on the inside, in osmotically equivalent amounts are used. This process takes place during actual measurement. A cell failing to develop high pressure is probably due to leakage, for a solution in a cell with a leaking membrane may exhibit a nearly constant pressure for a long time, thus giving one who has had little experience with membranes or one who gives them careless attention, the impression that he is measuring true maximum pressures. Semipermeable membranes are probably inversely related to the molecular weights of the substances whose pressures are measured (*i. e.*, a membrane may not leak with cane sugar but leaks very readily with glucose). Even in leaking cells, satisfactory measurements might be obtained by the differential method. The differential method consists in allowing the membrane to develop a constant pressure and then determine the concentration of the solution within and without the cell. This gives sufficient data for a correct interpretation.

The difficulties attending the work were now increased

by the appearance of a formidable assailant which manifested itself in the form of a minute vegetable organism known as penicillium. The development of ferments and the chemical changes attending their growth has been studied only to a limited extent. It, therefore, was necessary to obtain an efficient means of destroying these organisms which are extraneous in the development of *maximum* osmotic pressure. Necessity demanded that this poison should be effective in such small quantities that the pressure of the solutions should not be effected. Secondly, it must not act chemically, or otherwise upon the membrane, and lastly, is must not act chemically upon the solution. Possessing these three fundamental characteristics, it should also be able to prevent alcoholic fermentation. It thus appears that substances of an alkaline or acid nature were excluded from the outset. A series of experiments was undertaken with phenol, salicylic acid, thymol, hydrocyanic acid, chloroform and potassium cyanide, although no good results could be expected from the last. In the case of phenol, salicylic acid and potassium cyanide, a retardation in the growth was observed. However, a vigorous growth appeared later when penicillium was placed in a sterilized Pasteur's solution. Deleterious effects on the membrane were also noticed. It is possible that hydrocyanic acid might be used but the inconveniences accompanying its use eliminated it from consideration. Thymol was the only substance which seems to fully meet the demands. Thymol is very insoluble in water and a solution of one thousandth normal is found to be sufficiently concentrated to poison all growths of this kind.

Turning to more recent work on membranes and the porous cups in which they are deposited, it can be said that the method is essentially the same as that of the earlier workers. A cell is prepared for the membrane-forming process in the following way: A five-thousandth normal solution of lithium sulphate is placed in the cell and also in the jar in which the cell rests. It is connected to an electric circuit with electrodes of the same kind as previously

described. The air is then driven out of the cell wall by the endosmose of the sulphate solution which is electrolyzed. Lithium sulphate is used in place of potassium sulphate for the reason that the lithium ion is surrounded by a greater endosmose than the potassium ion. The electrodes for this work are made of platinum. The anode consists of a cylinder of platinum of sufficient size to surround the lower portion of the cell. The cathode is a smaller platinum cylinder which is fastened to a platinum wire passing through the rubber stopper at the same place as the funnel which admits solution into the cell. The funnel is of sufficient length to reach nearly to the bottom of the cell, thus carrying fresh solution to the bottom of the cell and forcing the old solution upward and outward through the siphon. The siphon is formed by a second glass tube which passes through the rubber stopper but bent at right angles to the funnel. These electrodes are now connected to a 110 volt circuit and the air is carried out by the large lithium ion.

The cell is placed in distilled water to remove any lithium salt that may have accumulated in the walls. The cell is now set up in the circuit, using distilled water and the remainder of the lithium salt is electrolyzed in the same manner as the air was removed, water being used instead of a sulphate solution. This electrolysis is continued until a minimum current is obtained. This minimum, in most cases, reaches about two ten-thousandths of an ampere. From this time on the cell is never exposed to the air for any length of time, nor is the unglazed portion ever handled by the worker. These precautions are manifestly necessary.

The real work of depositing the membrane is now ready to begin and a longer process is before the investigator. For the deposition of membranes, a tenth-normal solution of copper sulphate is used as the solution on the exterior and a tenth-normal solution of potassium ferrocyanide is used around the cathode. The cathode is a platinum cylinder and the anode is a copper cylinder in copper sulphate. Penicillium thrives very vigorously in copper sulphate and at this point it is necessary to take very great precautions.

If a new solution of copper sulphate in water is used, the deposition goes on satisfactorily. It is not always convenient to put a new solution of sulphate in the cup each time and to avoid the growth of penicillium it is found advantageous to make the copper sulphate solutions in thymol water of a concentration of one-thousandth normal. Thymol seems to effect electrolysis in no way and does not interfere with the deposition of the membrane. It prevents any growth of penicillium. The jar in which the copper sulphate solution is placed is held by means of suitable mechanical devices in a constant temperature bath, and the cell is allowed to dip into the copper sulphate solution to a short distance above the beginning of the glazed portion. The electrodes are arranged so that they are connected to fixed binding posts which are easily put in circuit carrying current and an ammeter for recording the current passing through the cell. Each time the cell is set up for deposition of membrane, the voltage is taken and the current read every fifteen minutes. This is done so that some idea of the behavior of the cell is known. Potassium ferrocyanide is poured into the cell by means of the funnel. The current is now turned on and the ions of copper meet the complex ferrocyanogen ions. A precipitate is thus formed, the position of which depends upon the nature of the porous cup. The solution of potassium ferrocyanide is renewed every three minutes to prevent the accumulation of alkali in the cell. This membrane-forming process is repeated for several days at a time in the first stages of the growth of a cell. The cell is then set up with a normal sugar solution containing eight hundred thirty nine ten-thousandths of a gram of potassium ferrocyanide to one hundred cubic centimeters of solution by weight. Potassium ferrocyanide is used with the sugar solution to repair any momentary ruptures. The object of setting a cell up in this way is to pack the membrane as firmly as possible and to fix it firmly in the wall of the cell. In addition, it ruptures the weakest parts of the membrane which are to be repaired the next time deposition of membrane takes place. It is fully realized that this small

amount of potassium ferrocyanide does not produce a complete repair of the ruptures nor is it believed that even in the finished cell is this repair complete; but it is believed that it hastens the formation of a membrane that approaches perfection because this repair takes place under pressure. On the supposition that the molecule of potassium ferrocyanide completely dissociates into five ions in solution "dilute and concentrated," it is considered that osmotically equivalent amounts of copper sulphate and potassium ferrocyanide are used. Consequently, the true osmotic pressure is not increased or decreased. A cell will probably develop fifteen to twenty atmospheres of pressure at this stage of its life history. It, however, would hardly be expected to maintain a constant pressure for more than twenty-four to forty hours.

Some approximate ideas as to the qualities of a cell are obtained from this trial measuremnt which is preferably carried on in a constant temperature bath. It is quite desirable that the cell be developed under uniform conditions. This statement is based on experimental evidence. No claim is made that it is definitely known in what manner the copper ferrocyanide membrane arranges itself in the pores of the cell but there is certain definite evidence at hand which has led to conclusions based upon physical and closely related analogies which will be discussed later. When the pressure decreases markedly, the cell is taken down, washed thoroughly with water at the same temperature as that at which it was used during the trial measurement. It is then placed in a solution of thymol inside and outside and allowed to soak for several hours. This thymol solution prevents the growth of penicillium which often infects the cell in which sugar is not completely removed and also removes any accumulated salt from the walls of the cell. The purpose of removing the accumulated salt will be fully discussed under the topic of cells giving constant ratios lower than should be expected under normal conditions.

During this first stage of membrane deposition, it is found that the resistance is very low at the outset but this increases

during the day, for we often deposit membranes for hours at a time when first working with a cell. The next day after shaking the resistance of the cell starts at about the same place but soon increases very rapidly, rising much higher than on the previous day. This change takes place repeatedly and soon it is found that a certain definite maximum resistance is reached for any particular cell. It must not be forgotten that often there are certain fluctuations in the resistance and these fluctuations are only eliminated as the process of membrane formation is continued. The higher the temperature, generally at which the cell is run, the lower the resistance. Cells, as a rule, whose membranes are deposited at forty degrees, do not show as high a resistance as those whose membranes are deposited at zero degrees. In some cases the resistance of membranes has been known to exceed one million ohms. Other cases are found in which a cell shows low resistance immediately after it has been taken down from a measurement.

The membrane is subjected to this packing and rupturing treatment repeatedly. Only trial measurements under uniform conditions are made. The second time a cell is set up for measurement, it begins to show characteristic traits. The investigator who becomes experienced with these variations, can form certain definite conclusions as to the relative excellency of the cells as a class. Usually, at this stage, imperfections show themselves and the cell takes a turn for better or worse at this point. Imperfections are due to two causes. The first cause of imperfection is a result of carelessness in the making of the cell. This manifests itself in small particles of iron or brass which come from the lathe which is used in turning out the cell. The clay is green (unbaked) and minute metallic particles adhere to it. (These particles are thrown about by the machinery which is used for the most part in metal work.) The unbaked cell goes to the potter and it is heated to a temperature, sufficiently high to fuse these particles. A piece of metal too small to be seen with the naked eye will produce a dark spot a couple of millimeters in diameter when fused. This

black spot serves as a nucleus about which copper collects. Instead of a membrane of copper ferrocyanide being formed, there is produced a spot of metallic copper. Osmotic activity decreases as the spot increases. The cell is usually discarded at this period of its life history. The second cause of imperfection is due to the fact that the cell is not placed in the furnace at the right temperature when it is fired. Small cracks are produced and these are not filled with glaze when the cell is refired. It is impossible to fill these cracks with membrane of sufficient compactness to hold high pressures.

The shortest period recorded of a cell that gave a measurement is found in the case of a cell, Z, by name, which developed into a good cell in the remarkably short period of thirty-eight hours. The usual period is two or three months. In some cases a period as great as six months is required. In others, the cell has never developed into a measuring cell. The length of time required to develop satisfactory membranes, depends very much upon the texture of the cell. At present, it can be said that about fifty per cent. of the number of cells worked with prove to be measuring cells.

The most interesting and important work connected with the measurement of osmotic pressure now begins. It is this part of the work which determines the success of the investigator in securing measurements. The cell is in its first stage of actual measurement and at this time the membrane should receive the greatest care. In order to carry out the work to the best advantage, three constant temperature baths were constructed. These baths are controlled automatically and keep temperature constant to within a few hundredths of a degree for periods of over a day. These baths are used for the deposition of the membrane at constant temperature and also to maintain constant temperature during the period of rest necessary for the cell. Much experience is required on the part of the investigator to know what treatment is most advantageous to the cell.

A systematic method of caring for the cells is also an important factor in the work. It has been found advisable to deposit membrane in all the cells for a period of two

hours, twice during the week. In addition, membrane is deposited in the cell for about an hour on the day on which the cell is to be set up for a measurement. The work is so planned that the manometer and the cell are put together as quickly as possible after the membrane has been deposited, with as little variation of temperature. All the solutions which in any way are to come in contact with the cell are kept at a constant temperature, the same as that at which the measurement is made. No variations in temperature are allowed to take place in any case where it can be avoided.

It has been found practicable in cells containing weak membranes to deposit the membrane at a higher temperature than that at which the measurement is to be taken. The most remarkable instance of such practice is found in the case of cell R which had given no measurements whatever. After treatment for nearly a week, it was tried out and gave a satisfactory measurement. It is now one of the most reliable cells in the laboratory. In order to avoid abrupt changes in temperature, the cell is placed in a solution of thymol of such volume as to cause a gradual change in temperature. Cell R had membrane deposited at 40° C., and then it was placed in thymol water at 40° C. This is now placed in a 25° bath and it slowly and gradually reaches a temperature of 25° because of the large volume of solution that must change in temperature. It will thus be seen that a membrane may be deposited at a temperature higher than that at which the measurement is to be taken but the reverse order cannot be carried out successfully. Instances in which these facts are clearly brought out are found in the cases of cells M, N, D and F, which were used at 5°. It required considerable time to develop them for 25° work.

No sudden or abrupt changes are allowed to take place during the period of rest of the cell. While the cell is resting, it is placed in a glass vessel and supported by an aluminium plate in which holes have been drilled. A thousandth normal solution of thymol is placed on the inside of the cell as well as in the vessel in which the cells rest. The purpose of this soaking is to remove any sugar solution which may

be occluded in the walls of the cell or to remove any accumulated salt such as potassium ferrocyanide or copper sulphate. The matter of removing accumulated salt is highly important since it may seriously affect the osmotic pressure of the solution being measured. Salt accumulates in the wall, due to too frequent use of the cell in taking measurements or insufficient soaking.

The type of cell used at the present time is made of a combination of clays from various sources. The process of making these cells has been described in an earlier paper. Each cell has a glazed and an unglazed portion. The upper part is glazed and hence it is not porous. The lower or unglazed portion is porous and it is in this portion that the membrane is deposited. During the deposition of membrane in the walls of the cell, it was previously stated that the ions of the two salts meet and form copper ferrocyanide. The current carries some of the salt along with it into the walls of the cell and here by capillary action, the solutions creep up under the glazed portion and meet at some point above the lowest portion of the glaze. The result is the formation of a membrane at those places where the ions chance to meet. However, there may not always be a meeting in this portion of the cell and only an accumulation of solution takes place. If a cell is not soaked for a considerable time, it is believed that there is a steadily increasing amount of salts left in the cell wall. This accumulation of salt will cause a ratio to be lower than should be expected under normal conditions but still it may be very constant. This may be explained by the fact that diffusion takes place counter to the osmotic activity and causes a constant decrease of the osmotic pressure. This accumulated salt will diminish the apparent osmotic pressure of a solution within the copper ferrocyanide membrane. Since its osmotic pressure is nearly constant, it is self evident that it will diminish the osmotic pressure of any given solution by a constant amount. This is one of the causes of low ratios obtained sometimes even though there is no loss in rotation of the solution form the cell. It will be admitted that a

sugar solution of a certain definite concentration will yield a constant maximum pressure due to osmosis. When this constant maximum is reached, water passes into the cell just as fast as water passes out or in other words equilibrium is established but suppose that this pressure toward the outside of the cell is exerted with constant value, then it becomes evident that there is a pressure acting opposite to osmotic pressure, which will produce a constant value below the normal value for that concentration. The amount that this value is below normal depends upon the amount of salt present and this in turn determines the osmotic pressure counter to that of the solution.

A second source of low measurements is obtained from imperfect membranes. They are termed imperfect because they do not behave normally. These imperfect membranes may be found in the cells that have been in service for a long time and seem to have lost their osmotic activity. Diffusion through such membranes is very slow and in some cases the pressure may increase for six or eight days. In the meantime, dilution has been taking place and now the cell shows signs of diminishing osmotic pressure. Then again little or no change in the pressure takes place, the pressure remaining the same as that exerted upon it mechanically. No reliance can be placed on measurements obtained from such cells. However, it may be said that such membranes may prove to be reliable at temperatures higher than those at which the work has been carried on. Another source of error lies in the fact that the porous part of the wall comes in contact with grease from the worker's hand in the process of setting up or in some other careless treatment. These cells cannot be repaired sufficiently to produce an osmotically active membrane because this grease interferes with the free passage of copper ions through the wall unless they are washed carefully with ether.

Still another source of error is found in the case of sugar solution containing potassium ferrocyanide, which is allowed to run on the exterior of the cell. It is then carelessly washed and there is formed a membrane of copper ferrocyanide on

the exterior of the cell as soon as the cell is placed in a copper sulfate solution. This forming of a membrane on the outer wall at any one time is small in amount, but the effect is accumulative unless care is taken in washing the cell off. It is found very bad policy to remove this membrane by dipping in sodium potassium tartrate solution. The proper method of preventing such difficulties is to use a tight fitting piece of thin rubber tubing which is slipped over the porous part of the cell. The overflow of solution is soaked up by means of drying paper; the cell is then washed with distilled water at a given temperature before placing into the copper sulfate. If all these little details are carefully observed, there is no reason why a membrance cannot be kept in active condition. Membranes which are out of sorts with the temperature at which they are used can in some cases be made active by depositing membrane in them at a temperature higher than that at which they are to be used.

Mention has already been made of the necessity of washing the cells carefully. Likewise, the vigorousness with which penicillium grows on almost any substance has received some attention in earlier paragraphs. To avoid these difficulties the copper sulfate used around the copper electrodes is made up with thymol water which seems to have no effect upon the electrolysis of the solution. In one instance the author found penicillium growing in copper sulfate at twenty degrees on the electrode itself. This is only further evidence concerning the fearlessness with which these organisms disseminate themselves. In such cases no other result could be expected than an infection of the cells by penicillium. This infection manifests itself more markedly at great dilutions than at those of greater concentration for the reason that penicillium will not grow in concentrated sugar solutions. It is not known in what manner these organisms act, nor have any hypotheses been advanced concerning their action. It is definitely known that something does take place to a greater or less degree depending upon the amount of infection. Manifestations of this diffi-

culty was observed at concentrations up to four-tenths normal sugar solutions. The solutions, taken from such cells, possess a more or less blue color and in every case there is a loss in rotation which means that some change has taken place in the sugar solution. What this blue color is due to is unknown at present. Work along this line is being carried out by the author. This infection, small as it was, continued for some time. It then occurred to the author that a saturated solution of thymol would hasten the extermination of these organisms. This treatment was tried on part of the cells and gave conclusive proof as to the advantages of the treatment. The cell was filled with this solution and set in a solution of the same strength. In about a week the infection was eliminated. Since the first experience with infection by penicillium, the cells are given a treatment once every week and no further evidence of infection has appeared. It might be interesting to know that thymol is soluble in only small amounts of water (1 : 1000 approx.). This is the degree of saturation which the solutions possess.

In earlier paragraphs it was stated that characteristics of cells would be discussed, and to this our attention is now turned. The rate at which lithium sulfate drives the air out of the cell gives the investigator an idea as to the porosity of the cell. Of course the porosity depends upon the compactness of the particles composing the cell. Burning at a high temperature increases the compactness. This is the reason for speaking of the hard-burned, non-porous type. A cell of this type will undoubtedly develop into a measuring cell more quickly than the open, porous kind because there are a greater number of plates to attach the membrane to and also the interstices are not as large and, consequently, they can be filled with a membrane sooner. The porous type have larger interstices which are to be filled with membrane. It is a fact that cells showing a high resistance usually behave better than those of lower resistance, but this is no criterion as to whether the cell will give a measurement. The matter of resistance is only a characteristic.

It is not understood why a cell shows these different resistances. Some membranes may show a resistance as high as a million ohms and not give a satisfactory measurement. Some cells develop pressure faster than others, but the exact reason of this activity is not known. However, it is a function of the membrane. Good normal membranes should hold a pressure of twenty-five atmospheres for a period of one hundred and sixty-eight hours with very little variation in the osmotic pressure. It is a matter of detail that corrections for atmospheric pressure are made in the calculation of osmotic pressure. If the atmospheric pressure increases, the total pressure of the cell would increase and *vice versa*. However, these changes do not take place at the same rate. The total pressure of the cell does not follow the barometer accurately.

In connection with the work at 25°, measurements lasting over very long periods of time were carried out with two views in mind. First, the characteristics of a normal membrane from the point of view of the length of time that it shows osmotic activity, and, secondly, to show that mechanical pressure does in no way influence our final osmotic pressure. However, mechanical pressure assists in the work by decreasing the length of time necessary to reach a maximum pressure. In one case an experiment lasted over a period of 536 hours with the greatest variation in ratio of osmotic to gas pressure of two points in the third decimal place. After a moment's thought, it will appear that this is really a remarkable measurement considering the wide variations of barometric pressure for a period of two weeks or more. Other experiments lasting from 150 to 200 hours have been carried on with even better results. In one of these experiments, the greatest variation in ratio was only one point in the third decimal place for a period of 192 hours. This, in brief, gives an idea of the possibilities of a good membrane and also a sufficient reason for retaining cells which are of the right texture to develop a membrane of this magnitude.

The question may arise as to the location of this membrane

which is deposited in the cell. The only answer to this question is indefinite at best. There are many possibilities as to the place that this membrane may be formed. It all depends upon the concentration of the solutions and also the place at which the ions meet. Considerable work has been done along this line to secure the proper adjustment of the concentrations. It is obvious that the formation of a membrane on the outer wall of the cell can have little or no support whatever against the pressure from within. The fact is, that cells in which the membrane has been deposited upon the inner edge of the wall have been found to be uniformly much more active than those in which the membrane was found within the wall. This is to be expected as diffusion takes place comparatively slowly within a porous body of close texture and considerable density. If, on the other hand, the membrane is on the inner edge of the wall, the practically undiminished concentration of the solution within, and the pure water circulating through the porous wall, are separated only by a thin membrane, and the maximum flow of water will be observed. Ionic velocities and dissociation of electrolytes play an important rôle in fixing the position of the membrane. If the membrane is not close enough to the wall, it will peel off very easily, for the reason that it has no opportunity to attach itself.

Through accident to the cells, it has been possible to examine cells which possesss membranes of extraordinarily good qualities. Cell G, as it was called, had the bottom split off, due to a very sudden change in temperature, and gave an opportunity to examine its membrane. It was found that the membrane was deposited very close to the inner wall, vertically and horizontally as well. Extending into the wall a fraction of a millimeter, a brownish coloration is distinctly perceptible. In addition, there was found the same brownish coloration up under the glazed portion of the cell. This is the situation of the membrane proper, but there may also be a reddish color on the exterior of the cell. It may be said that this is a product of probable care-

lessness for the reason that it may be avoided by using proper precautions. It is detrimental because it retards outward diffusion of water. It may be prevented by keeping potassium ferrocyanide from coming in contact with the outer wall, which is filled with copper sulfate during the process of membrane deposition. Thus copper sulfate can only be removed by continued soaking. The formation of this membrane on the exterior of the cell is only further evidence for the care that should be exercised in running the cells. Another important observation in connection with the characteristics of membranes is the slowness with which they respond to barometric changes, when the membrane has become dense, or if excess mechanical pressure has been exerted on the membrane, it returns very slowly to its normal position. As a rule it does not remain at constant pressure, but continues its fall, which indicates that dilution is taking place due to leakage. During this present year it was necessary to go from zero degrees up to twenty-five for measurements. Great difficulty was experienced in making this change. It required nearly a month and a half to get these membranes in suitable condition for measurement.

Cells become inactive due to a large amount of membrane. They fail to give measurements, and it is highly important that a method for recovering them should be devised. Various reagents will dissolve the copper ferrocyanide, but it is also found that they attack the cell itself, rendering it valueless for deposition of membrane a second time. Mineral acids have been tried with no success whatever. Tartrate solutions do not remove the membrane entirely. The only method which is known to be successful is the electrolytic. High voltages were tried, but it was found that the cell became very hot due to its own resistance. The voltage which seemed most suited to the work was obtained from twenty storage cells connected in series. The danger of heating the cell lies in the fact that it may crack if it is not carefully watched. In the case of low voltage it is possible to allow the process to go on night

and day. The copper collects on the cathode and thus is removed by dipping into nitric acid. A little tartaric acid is used to add to the conductivity of the solution. It has been found that about two months are required to remove the membrane. The cell is then sent to the potters and refired, in a manner similar to the first process. Membrane is then deposited in the cell just as in a new cell. The same amount of time is necessary and the same attention is needed to develop this cell into a measuring cell. The experiment has been tried with cells "A" and "C," both of which have given measurements. The process is being tried on "J" and "K." If good results are obtained from these cells upon redeposition of membrane, it is conclusive that the method is satisfactory.

NOTE 1.—During the vacation the cells were placed in a solution of thymol. No attention was given them except that the solution of thymol was renewed at intervals.

*Indicates that the maximum resistance on the day after a measurement had been taken was that indicated by the sign *

In the accompanying tables, the date on which the deposition of membrane began is indicated at the top of each column under the name of the cell in question. Under this, the date on which the cell gave its first measurements, is found. In the first vertical column the days on which the cell was set up for deposition of membrane previous to its first measurement; in column 2, the number of hours during which deposition of membrane took place on any given date; third column, the maximum resistance for that day, are tabulated.

Looking over the table for any cell, it will be found that usually a minimum resistance was recorded on the day on which the cell was taken down from a trial measurement. The cause of this low resistance is entirely unknown. Certain hypothesis might be suggested, but owing to the fact that the changes taking place in the membrane cannot be observed, no definite statements will be made. Another feature brought out by the tables is the fact that some cells

Cell Z.
Began deposition March 10, '09.
First measurement, Feb. 5, '09.

Date.	Hours.	Resistance.
Mar. 10	6	216,000
" 11	4	140,000*
" 12	3	180,000
" 15	6	125,000*
" 16	7	216,000
" 18	3	106,000*
" 19	4	60,000*
" 20	5	186,000
" 22	6	220,000
" 23	8	188,000*
" 25	8	155,000*
" 26	8	290,000
" 29	4	160,000*
Apr. 1	2	183,000
" 2	2	160,000*
" 5	3	187,000
	16 measurements	

Cell C_3.
Began deposition Oct. 15, '09.
First measurement, Feb. 23, '10.

Date.	Hours.	Resistance.
Oct. 15	1	375,000
" 20	2	290,000
" 21	2	140,000*
" 22	3	150,000
" 25	1	220,000
" 26	2	210,000
" 27	1	183,000*
" 29	1	230,000
Nov. 15	2	185,000*
" 24	1	350,000*
" 29	1	357,000
Dec. 1	1	1,080,000*
" 6	3	535,000*
" 13	3	560,000
Jan, 6	3	275,000*
Feb. 16	4	550,000
" 23	2	110,000*

Cell W.
Began deposition Mar. 24, '09.
First measurement, Oct. 19, '09.

Date.	Hours.	Resistance.
Mar. 24	4	110,000
" 26	8	290,000
" 29	4	113,000*
" 30	3	220,000
Apr. 1	2	486,000*
" 2	3	400,000
" 6	4	140,000*
" 8	4	160,000
" 14	4	224,000
" 16	7	160,000*
" 19	3	140,000
" 23	2	130,000*
" 24	4	184,000
May 10	2	160,000*
	Note.	
Oct. 5	1	189,000
" 6	3	275,000
" 9	3	565,000
" 11	2	180,000*
" 13	2	280,000
" 15	1	275,000*

Cell I_3.
Began deposition, May 20, '09.
First measurement, Mar. 7, 1910.

Date.	Hours.	Resistance.
May 20	3	60,000
Oct. 9	3	285,000
" 13	2	157,000*
" 20	2	387,000
" 21	2	555,000
" 26	1	272,000
" 29	1	380,000
Nov. 9	1	380,000
" 15	1	275,000*
" 22	1	550,000
" 29	1	535,000
Dec. 13	3	1,120,000
Jan. 6	2	550,000*
" 31	1	280,000
Feb. 11	1	280,000*
" 16	2	550,000
Mar. 7	3	550,000

Cell G.
Began deposition, May 20, '09.
First measurement, Jan. 24, '10.

Date.	Hours.	Resistance.
May 20	4	80,000
" 22	4	133,000*
Oct. 13	2	220,000
" 18	1	275,000
" 20	2	194,000*
" 21	2	275,000
" 27	1	224,000*
Nov. 9	2	265,000*
Dec. 4	2	355,000
" 17	1	550,000
Jan. 6	1	220,000*
" 22	2	365,000
" 24	2	220,000

Cell A_3.
Began deposition, May 4, '09.
First measurement, Feb. 12, '10.

Date.	Hours.	Resistance.
May 4	3	140,000
" 6	3	160,000
" 8	3	183,000
" 11	2	270,000
" 13	3	220,000
" 17	2	220,000
" 18	2	222,000
" 20	2	90,000
" 22	3	180,000
	Note.	
Oct. 9	3	160,000
" 13	2	275,000
" 18	1	275,000
" 20	2	290,000
" 21	2	278,000
" 27	1	183,000
Nov. 9	2	350,000
" 29	1	535,000
Dec. 1	1	540,000
Jan. 6	3	550,000
" 31	1	560,000
Feb. 11	1	280,000

Cell R.
Began deposition, Feb. 3, '09.
First measurement, Mar. 21, '09.

Date.	Hours.	Resis tance.
Feb. 3	2	275,000
" 5	3	365,000
" 8	2	545,000
" 10	3	297,000*
" 12	5	113,000*
" 13	3	224,000
" 16	2	355,000
" 17	2	53,000*
" 19	2	363,000
" 25	6	285,000
Mar. 2	6	525,000
" 11	1	250,000*
" 24	2	14,000*
Apr. 2	1	160,000*
" 9	3	280,000
" 20	2	375,000
" 27	1	375,000
May 12	2	36,000
" 22	1	265,000*
	Note I.	
Oct. 9	3	565,000
" 11	2	372,000
" 14	2	1,120,000
Nov. 4	2	550,000
" 29	1	535,000
Dec. 9	2	333,000
Jan. 31	1	565,000
Feb. 11	1	550,000
Mar. 2	1	98,000
" 12	2	1,000,000
" 21	1	28,200

14 measurements

Cell V.
Began deposition, Mar. 10, '09.
First measurement, Nov. 29, '09.

Date.	Hours.	Resistance.
Mar. 10	6	108,000
" 11	4	110,000
" 12	3	138,000
" 15	6	140,000
" 16	7	154,000
" 18	3	130,000
" 19	4	155,000
" 20	5	160,000
" 22	6	180,000
" 23	8	100,000
" 26	8	195,000
" 29	4	125,000
" 31	3	160,000
Apr. 1	2	160,000
" 2	3	110,000
" 6	4	160,000
" 8	4	186,000
" 9	3	140,000
" 14	4	187,000
" 16	7	187,000
" 24	4	170,000
	Note.	
Oct. 11	2	280,000
" 13	2	280,000
" 14	2	280,000
" 15	1	560,000
Nov. 4	4	33,000
" 5	1	535,000

Cell A_5.
Began deposition, May 4, '09.
First measurement, Feb. 28, '10.

Date.	Hours.	Resistance.
May 4	3	110,000
" 6	4	175,000
" 8	3	110,000
" 11	2	155,000
" 14	4	140,000*
" 17	4	132,000
" 18	3	116,000*
" 20	3	65,000*
" 22	3	150,000
	Note.	
Oct. 9	3	140,000
" 13	2	275,000
" 20	2	194,000
" 21	2	185,000
" 26	1	135,000*
Nov. 1	2	157,000
" 6	2	180,000*
" 11	1	185,000
" 12	1	185,000
" 19	2	350,000
Dec. 8	1	330,000
" 18	1	187,000*
Jan. 11	1	232,000
" 31	1	187,000*
Feb. 14	1	220,000
" 21	1	184,000*
" 25	1	200,000
" 28	1	214,000*

Cell P_3.
Began deposition, Mar. 10, '09.
First measurement, Apr. 14, '09.

Date.	Hours.	Resistance.
Mar. 10	6	108,000
" 11	4	160,000
" 12	3	12,000
" 15	6	30,000
" 16	7	135,000
" 18	3	133,000
" 19	4	180,000
" 20	5	160,000
" 22	6	157,000
" 23	8	190,000
" 25	8	156,000
" 26	8	234,000
" 29	4	140,000
" 30	3	224,000
Apr. 1	2	187,000
" 2	3	40,000
" 6	4	185,000
" 7	1	285,000
" 8	4	123,000
" 12	2	280,000
" 14	4	190,000

require a greater number of hours to produce a firm membrane than others. This, for the most part, is due to the texture of the cell which has previously been described under cell characteristics.

In no case has a cell given a satisfactory measurement previous to that indicated under each cell. The resistances of each cell are recorded every fifteen minutes and only the maximum values are observed in the accompanying tables. These cells have not consistently given measurements after the first time. Various causes have been responsible for these variations. The best cells may not give more than eight or ten good measurements in a year for the obvious reason that each cell is allowed a period of rest ranging from one hundred and fifty to three hundred hours and also making due allowance for an occasional failure on the part of the cell to respond to the work required of it. Changing from one temperature to another also occasions considerable delay.

It is hoped that the carefully tabulated variations of the behavior of a cell will throw some light on the future care and treatment of the cells. It may offer some means of improving the present methods of deposition and lead to a satisfactory explanation of the fluctuations observed in the case of any particular cell. Hydrocyanic acid has been found a satisfactory means of removing penicillium from the cell, while formaldehyde is an effective means of preventing the growth of these organisms in the containing vessels where measurements are taken. Furthermore, it has been found that penicillium uses up the membrane and leaves a blue color. No definite statement can be made regarding the manner in which it acts.

BIOGRAPHY.

Chester Newton Myers was born in Lansingburgh, New York, on November 7, 1884. His early education was received in the public schools of Valley Falls, N. Y. June, 1906, he received the degree of Bachelor of Arts from Williams College. He was then appointed instructor of Physics and Chemistry at the Cattaraugus High School, which position he held till entering Johns Hopkins University. In addition to holding the position of instructor, he was assistant principal of the high school. In October, 1908, he entered Johns Hopkins University as a graduate student in Chemistry. In 1909–1910 he held a University scholarship. His minor subjects are Physical Chemistry and Physics.